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QUANTITATIVE DETERMINATION OF A HYDROGEN IMPURITY IN A SODIUM COOLANT BY HYDRIDE THERMAL DISSOCIATION

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16 Abstract
Molten Na containing H was heated in a vacuum at 450°, the gases evolved were pumped through a liq-N trap and the H_2 was then oxidized on Cu oxide heated to 400°. The accuracy of the method is 1.5% and the sensitivity is 1 x 10^{-5} wt % H.

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QUANTITATIVE DETERMINATION OF A HYDROGEN IMPURITY IN A SODIUM COOLANT BY HYDRIDE THERMAL DISSOCIATION

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Under the existing laboratory methods of analyzing hydrogen content in sodium [1 - 3] a sample is taken from a loop, cooled and transported into analytical apparatus. These operations also result in contamination of the metal in the sample or disappearance of the impurity, for example, as a result of its redistribution during hardening of the metal. /227*

Among the most famous methods of quantitative determination of hydrogen are: method based on selective hydrogen diffusion through metal partitions [4], and the method based on the dependence of electrical resistance of molten sodium on its hydrogen content [5].

This article describes the method of determining hydrogen content in sodium based on hydride thermal dissociation during vacuum distillation of a sodium sample, interaction of the released hydrogen with cupric oxide and manometric measurement of the quantity of formed water.

The main source of hydrogen impurity in a sodium coolant is sodium hydroxide formed during interaction of sodium with water or water vapor. With a high temperature and sodium surplus, hydroxide breaks down forming oxide and sodium hydride. The thermal threshold of this reaction is about 300°C [6]. In contrast to other nonmetallic impurities (oxides, carbides, carbonate, etc.), sodium hydride has a relatively high dissociation pressure. Sodium hydride dissociation elasticity in the temperature interval 100 - 600°C is satisfactorily described by the equation [7, 8]:

$$\lg P_{\text{г}} = -\frac{6100}{T} + 11.61, \qquad (1)$$

*Numbers in margin indicate pagination in original foreign text.

where P_g is measured in millimeters of mercury column.

Hydrogen equilibrium pressure above liquid sodium containing soluble sodium hydride rises with an increase in the hydride content in sodium until the solution reaches a saturation state. The solid phase (hydride) further begins to crystallize out of the melt. Hydrogen pressure above the melt becomes unchanged and equal to the dissociation elasticity of pure hydride.

Publication [8] has shown that hydrogen solubility of sodium is proportional to the square root of hydrogen partial pressure above the melt:

$$C = k\sqrt{P}, \tag{2}$$

Correspondingly

$$C_s = k\sqrt{P_s}, \tag{3}$$

where C_s is hydrogen content in a saturated solution at a specific temperature.

The dependence of C_s on T [8] is expressed by the correlation

$$\lg C, \text{wat\%}\ H_2 = -\frac{2880}{T} + 2.2. \tag{4}$$

In closed circulation systems under isothermic conditions, hydrogen equilibrium distribution was established between the melt and the gas cavity filled with inert gas. This equilibrium is determined by the quantity of metal, the total content of impurity in the system, the volume of the gas cavity and temperature. Change in any of these parameters leads to a redistribution of the hydrogen impurity in the loop between the metal and the gas cavity [5].

Hydrogen distribution in the loop can be characterized by the distribution coefficient expressing the ratio of hydrogen concentration in metal C to its concentration in the inert gas of the gas cavity C_r. It follows from equation (2) and (3) that at constant temperature, the dependence of hydrogen pressure above the melt on its concentration in the melt can be represented by the correlation

$$P = P_g \left(\frac{C}{C_s}\right)^2. \qquad (5)$$

Using the equation for the state of ideal gas in correlation (5), we obtain an expression for the distribution coefficient:

$$k = \frac{C}{C_r} = \frac{C_s RT}{\sqrt{P_g P}}. \qquad (6)$$

at a concentration corresponding to the saturation state $C = C_s$, $P = P_g$, while $C_r = C_r^{\text{макс}}$. The hydrogen impurity equilibrium between the saturated melt and the gas cavity is determined by the distribution coefficient according to the expression /228

$$k_s = \frac{C_s}{C_r^{\text{макс}}} = \frac{C_s RT}{P_g}. \qquad (7)$$

The calculated values of the quantity C_s are presented below:

T° C	k_s	T° C	k_s
100	$2.5 \cdot 10^4$	250	$1.0 \cdot 10^2$
150	$2.4 \cdot 10^3$	300	32
200	$4.4 \cdot 10^2$	400	5.3

We find from (6) and (7) that

$$k = k_s \sqrt{\frac{P_g}{P}} = k_s \frac{C_s}{C}. \qquad (8)$$

The equilibrium distribution of hydrogen impurity between the metal and inert gas determines the possible implementation of two methods of quantitative determination of impurity content in the sodium by analyzing the metal sample and contents of gas cavity. We have developed a method and apparatus for chemical and technological quantitative determination of the hydrogen impurity directly in the melted sodium sample.

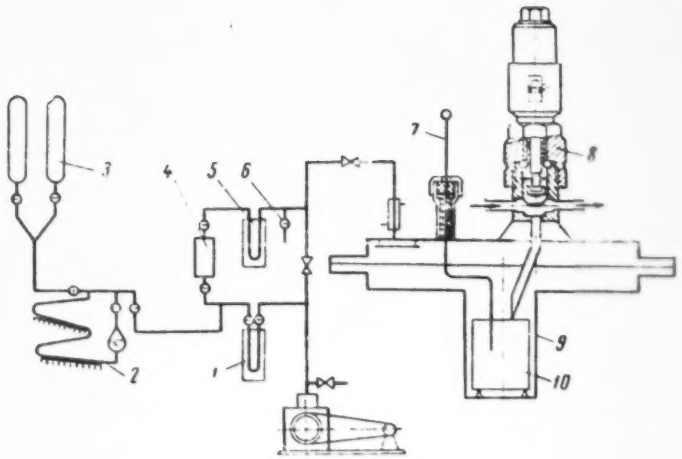

Figure 1. Scheme for Analytical Unit with Sample-Taking Distiller

The samples were taken and distilled using a sample-taking distiller installed in an experimental test stand loop. The test stand was equipped with a device for introducing gaseous hydrogen into the sodium. A section for measuring electrical resistance of liquid sodium [5] was installed on one of the test stand bypasses. Sodium circulated by electromagnetic pump with flow up to 1 m^3/h.

Figure 1 presents a scheme for analytical unit with sample-taking distiller that allowed successive taking and distilling of 4 - 5 sodium samples without opening the sample-taker. Before taking the first sample, the inner surface of the sample-taking distiller was purified of traces of adsorbed moisture by taking the small quantity of sodium (3 - 5 g) and distilling it at a temperature 450°C for 1 h. The sample was taken through drain valve 8 into molybdenum vessel 10 in which the sodium was distilled. Monitoring the melt level in the vessel by a mobile contact level gauge 7, we could monitor all the samples 5 - 100 g. Distiller 9 was heated by crucible electric furnace whose temperature (450°C) was maintained automatically during the entire sample distillation time. The sample-taking distiller was connected to a glass analytical unit. The gases released during

sodium sample distillation were constantly pumped out (with a vacuum about 0.01 mm Hg) into an analytical unit. The gases in it passed through trap 5 cooled by liquid nitrogen in which water vapors and carbon dioxide were frozen. Hydrogen was oxidized by cupric oxide in reaction vessel 4 heated to 400°C. The water formed in this case was frozen in trap 1 cooled by a mixture of 2/3 alcohol and 1/3 liquid nitrogen to temperature 90 ± 5°C. The quantity of frozen moisture was then determined with heating of trap 1 using a Z-shaped oil-filled manometer 2. The moisture quantity was measured with sensitivity 0.008 cm^3 per 1 mm of manometer scale. When additional containers 3 connected to the analytical vessel with high hydrogen contents in the sample were used, the sensitivity was 0.05 cm^3 per 1 mm of scale. The measurement part of the analytical unit was graduated by dosing valve 6. The efficiency of the analytical part of this device was checked by adding a dosed quantity of hydrogen. The experiments demonstrated that the introduced quantity of hydrogen was determined with relative accuracy 1.5%.

As shown by thermodynamic calculation (Figure 2), even at very low hydrogen pressures in the system there is a possibility of /229 thermodynamic interaction between hydrogen and the concentrated sodium, although it is weak. This phenomenon could distort the results. Special experiments were conducted to analyze sodium samples containing an a priori known quantity of hydrogen introduced into a sodium sample in a hydroxide form. The results of 22 experiments demonstrated that when 100 - 200 kg of hydrogen were added as sodium hydroxide into a sodium sample weighing 20 g, the accuracy of hydrogen analysis is characterized by root-mean error about ±15%. One can draw the conclusion that there is essentially no interaction between hydrogen and sodium sublimates. During sodium distillation, hydrogen partial pressure in the system could be so slight that hydride formation on sublimates becomes negligible. In addition, with constant evacuation of the system there is an irreversible shift in equilibrium towards hydride dissociation. It is also known that hydrogen interaction with liquid sodium begins at a temperature about 200°C [9]. Condensate temperature (100°C) could therefore be insufficient to overcome the activation

threshold of this chemical reaction.

Experiments were conducted to compare the results of analysis with readings of an instrument operating on the principle of dependence of sodium electrical resistance on hydrogen content. The method of electrical resistance permits monitoring of the hydrogen concentration from the sodium coolant with sensitivity 3.3×10^{-5}% by weight of H_2 per division of standard direct current bridge [5]. An additional quantity of hydrogen was added to the loop with sodium in which the initial hydrogen content was 6×10^{-4}% by weight to draw a comparison. Increment with hydrogen concentration in liquid sodium was recorded by both methods with a change in concentration of 50×10^{-4}% by weight. The difference in indicator readings for electrical resistance and results of analysis by methods of thermal dissociation does not exceed ±10%.

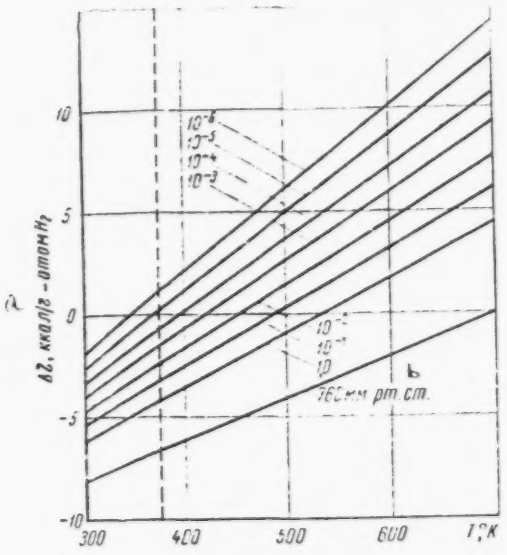

Figure 2. Dependence of Isobaric-Isothermic Potential of Sodium Hydride Dissociation Reaction on Temperature with Different Hydrogen Pressures in System (Key on next page)

Figure 2. Key:
a. kcal/g-atom H_2
b. mmHg

The measurement part of the unit for determining hydrogen permits a measurement of very slight quantities of gas (less than 0.01 cm^3). The method sensitivity is limited, however, by the result of the control test and with multiple reliable analysis of the latter, it is limited by the error of conducting it. It could be considered that the accuracy of the controlling experiment as applied to this analytical method is determined by that quantity of hydrogen which for some reason is detected constantly when there is no sodium sample in the sample-taking distiller. Hydrogen was analyzed for this purpose before the series of successive 4 - 5 analyses and after them under conditions of an established distillation mode but in the absence of a sodium sample. The quantity of hydrogen found was a correction for the control experiment. Several series of these experiments led to the following correction quantities for the control experiment:

Номер измерения[a]	Количество водорода, $см^3$[b]	Номер измерения[a]	Количество водорода, $см^3$[b]	Номер измерения[a]	Количество водорода, $см^3$[b]
1	1,80	8	1,83	15	2,70
2	1,76	9	1,72	16	3,70
3	1,76	10	3,07	17	1,23
4	1,85	11	2,30	18	1,28
5	0,81	12	2,40	19	0,75
6	1,77	13	2,70	20	1,80
7	1,83	14	1,35	21	2,76

Key:
a. number of measurement
b. quantity of hydrogen, cm^3

It follows from these data that the average arithmetical magnitude for the control experiment correction equals 1.93 cm^3. The root-mean-square error in determining an individual quantity of the control experiment is 0.66 cm^3. The error in determining an individual quantity

of the control experiment is that accuracy with which the minimum quantity of hydrogen and sodium can be analyzed. It consequently characterizes sensitivity of the method implemented by the described apparatus. Sensitivity of the analyses in calculation for 75 g of sodium sample is 8 x 10^{-5}% by weight of hydrogen. /230

TABLE. RESULTS OF EXPERIMENTS TO DETERMINE ERROR IN METHOD REPRODUCIBILITY

a Номер серии	b Номер анализа	c Количество водорода $\times 10^{-4}$, вес.% (в пересчете на пробу натрия 75 г)	d Среднеквадратичная ошибка воспроизводимости, вес.%
1	1	4,0	$\pm 1 \cdot 10^{-4}$
	2	2,6	
	3	1,8	
	4	4,8	
	5	2,0	
2	1	2,5	
	2	2,7	
	3	2,9	
3	1	5,3	
	2	5,8	
4	1	12,4	$\pm 3 \cdot 10^{-4}$
	2	17,4	
	3	12,5	
5	1	42,0	
	2	38,0	

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Key:
a. number of series
b. number of analysis
c. quantity of hydrogen x 10^{-4}, % by weight (in conversion for 75 g of sodium sample)
d. root-mean-square error of reproducibility % by weight

In order to improve the method sensitivity, the metal sample should be enlarged. With 600 g of sodium sample, analysis sensitivity of hydrogen equalled 1 x 10^{-5} % by weight. Analysis of this metal

sample purified using a cold diffusion trap indicated a hydrogen content equal to 4×10^{-5} % by weight.

Method reproducibility was determined by analyzing several series of parallel sodium samples. The magnitude of the reproducibility quantity was found by a technique described in publication [10]. The results of these analyses presented in the table demonstrate that the magnitude of reproducibility error depends on hydrogen content in sodium. In the concentration interval $(2 - 6) \times 10^{-4}$ % by weight, the root-mean-square error of reproducibility is ± 0.8 cm^3 (1×10^{-4} % by weight in conversion for 75 g of sodium sample). It is close to the root-mean-square error of determining the magnitude of the control experiment. This indicates that at low concentrations, the error is mainly determined by the error in the control experiment magnitude. In the concentration interval $(12 - 40) \times 10^{-4}$ % by weight, the root-mean-square error of reproducibility is ± 2.4 cm^3 which corresponds to 3×10^{-4} % by weight with sample of 75 g. Apparently with a higher hydrogen content additional sources of error appear. Their origin has not been precisely established.

The developed method of analyzing hydrogen in sodium can be successfully employed to analyze the other alkaline metal-coolants. Preliminary experiments demonstrated the possible applicability of the method to analyze lithium. A positive aspect of this method is the possibility of simultaneous analysis of several nonmetallic impurities in alkaline metal sample. The use of the sample-taking distiller permits simultaneous analysis in the sample of hydrogen as a product of dissociation during metal distillation, and oxygen remaining in the residue as oxide after distillation. The use of gas chromatography for sample analysis of the gas components released during distillation of the alkaline metal sample could significantly expand the potentiality of this method.

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